Lithium monoxide anion: A ground-state triplet with the strongest base to date

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Lithium monoxide anion (LiO^-) has been generated in the gas phase and is found to be a stronger base than methyl anion (CH_3^-). This makes LiO^- the strongest base currently known, and it will be a challenge to produce a singly charged or multiply charged anion that is more basic. The experimental acidity of lithium hydroxide is ΔH°_{acid} = 425.7 ± 6.1 kcal·mol^{-1} (1 kcal = 4.184 kJ) and, when combined with results of high-level computations, leads to our best estimate for the acidity of 426 ± 2 kcal·mol^{-1}.

computations | mass spectrometry | super base

The gas-phase acidities of the hydrogen halides were first reported via the application of a thermodynamic cycle (Eqs. **1**–**5**) in 1942 by Briegleb (1, 2).

$$HX \rightarrow H^\cdot + X^\cdot \qquad BDE(HX) \qquad [1]$$

$$H^\cdot \rightarrow H^+ + e^- \qquad IE(H^\cdot) \qquad [2]$$

$$X^\cdot + e^- \rightarrow X^- \qquad -EA(X^\cdot) \qquad [3]$$

$$HX \rightarrow H^+ + X^- \qquad \Delta H^\circ_{acid}(HX) \qquad [4]$$

$$\Delta H^\circ_{acid}(HX) = BDE(HX) + IE(H^\cdot) - EA(X^\cdot) \qquad [5]$$

In subsequent years, the acidities of thousands of compounds have been measured by using a variety of techniques (3), and the acidity scale currently spans a 125 kcal·mol^{-1} (1 kcal = 4.184 kJ) range from CH_4 (ΔH°_{acid} = 416.8 ± 0.7 kcal·mol^{-1}) (4, 5) to $HN(SO_2C_4F_9)_2$ (ΔH°_{acid} = 291.1 ± 2.2 kcal·mol^{-1}) (6) [see supporting information (SI) *Text*]. Methyl anion is the strongest base currently known, which is a position it has occupied for the past 30 years. This raises the question as to whether a more basic species can be made. In this article, we use sophisticated experimental techniques and state-of-the-art theoretical calculations to show that the lithium monoxide anion (LiO^-) is in fact more basic than methyl anion, and that it will be a challenge to produce a species that is still more basic.

Alkyl groups are polarizable but also are generally electron-releasing and, depending on which influence is larger, can destabilize anions. Kinetic measurements indicate that ethane and the secondary position of propane [$(CH_3)_2CH_2$] are 2–3 kcal·mol^{-1} less acidic than methane (7), but their conjugate bases have never been observed (8, 9). This is not surprising because the electron affinity of methyl radical is only 1.8 ± 0.7 kcal·mol^{-1} (4), and $CH_3CH_2^-$ and $(CH_3)_2CH^-$ are predicted to be unbound with respect to electron detachment (7). Electronegative substituents stabilize negative ions and increase acidities, as reflected by the first-row hydrides [i.e., HF (most acidic) > H_2O > NH_3 > CH_4 (least acidic)]. To decrease the acidity of a compound and make a stronger base, one might employ an electropositive substituent such as lithium. However, the conjugate bases of lithiated compounds are difficult to prepare in the gas phase, and almost nothing is known about them because the neutral acids tend to be involatile, moisture sensitive, and pyrophoric.

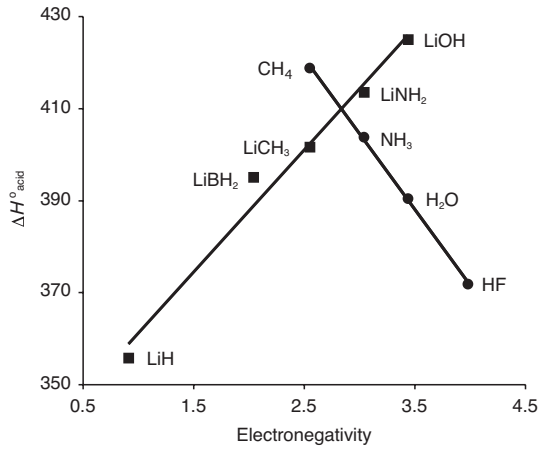
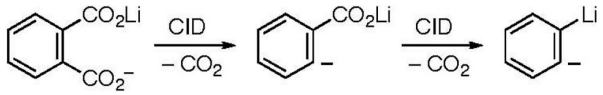


Fig. 1. Gas-phase acidities of first-row hydrides (HX) and their lithiated analogs versus Pauling electronegativities of X [circles, experimental values (14); squares, BD(T)/aug-cc-pVQZ theoretical values obtained in the present study].

A general method for producing metal-containing anions that overcomes these practical problems was developed by Bachrach, Hare, and Kass (10) and subsequently exploited by O'Hair *et al.* (11–13). In this approach, metal salts of dicarboxylates are produced by electrospray ionization (ESI) and fragmented via energetic collisions (CID), thereby leading to the sequential expulsion of two molecules of carbon dioxide but retention of the metal ion. For example, the conjugate base of phenyllithium was formed from the lithium salt of 1,2-benzenedicarboxylate, as shown in Eq. **6**.



[6]

This methodology provides a predictable and rational means for making ions that are difficult to prepare in other ways. In this article, we report its use to synthesize LiO^- and determine the acidity of lithium hydroxide via Eq. **5** because our preliminary high-level computations indicated that the LiO^- ion is extremely basic.

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The authors declare no conflict of interest.

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Table 1. Computed BD(T)/aug-cc-pVQZ and CAS-AQCC/aug-cc-pVQZ acidities of HX at 298 K

HX	ΔH°_{acid}, kcal·mol^{-1} BD(T)	AQCC	Experimental
$LiBH_2$	395.1	393.7	
$LiCH_3$	401.6	402.8	
$LiNH_2$	413.5	414.7	
LiOH	425.0	426.2	
LiSH	375.8	376.0	
LiH	355.8	356.3	356.0 ± 0.1*
BeH_2	393.4	395.9	
BH_3	412.1	412.2	
CH_4	418.8	419.2	416.8 ± 0.7†
Li_2BH	385.3	384.8	
Li_2CH_2	399.8	400.1	
Li_2NH	417.6	419.7	
$NaCH_3$	401.2	402.0	
NaOH	418.6	419.7	
NaSH	382.0	381.5	
NH_3	403.7	404.9	403.4 ± 0.1‡
H_2O	390.4	394.1	390.27 ± 0.02‡
HF	371.8	374.1	371.331 ± 0.003‡

*Ref. 3.
†Ref. 4.
‡Ref. 14.

Results and Discussion

Electronegative substituents are well known to stabilize negative ions and increase acidities, and this is reflected in a plot of ΔH°_{acid}(HX) vs. the electronegativity of X for first-row hydrides (Fig. 1) (14). Electropositive substituents such as lithium and sodium might be expected to show the opposite behavior, but BD(T)/aug-cc-pVQZ [referred to simply as BD(T) hereafter; see *Theoretical Procedures*] calculations on methyllithium (ΔH°_{acid} = 401.6 kcal·mol^{-1}) (15) and methylsodium (ΔH°_{acid} = 401.2 kcal·mol^{-1}) indicate that both of these substrates are 15–16 kcal·mol^{-1} more acidic than methane. In other words, these alkali metal substituents lead to enhanced acidities in these cases. However, the opposite effect can also be observed. For example, substitution of a lithium for a hydrogen in ammonia and water leads to weaker acids [i.e., ΔH°_{acid} = 403.4 ± 0.1 (NH_3) vs. 413.5 [$LiNH_2$, BD(T)] and 390.27 ± 0.02 (H_2O) vs. 425.0 [LiOH, BD(T)] kcal·mol^{-1}], which also are predicted to be less acidic than methyllithium. This reflects the acidities of lithiated compounds, which display the opposite trend to that of first-row hydrides with Pauling electronegativity values (Fig. 1) (16). Because LiO^- is computed to be 6.2 kcal·mol^{-1} [BD(T)] more basic than CH_3^- (see Table 1) and is predicted to be a ground-state triplet ion, this diatomic anion represents an interesting but challenging experimental target.

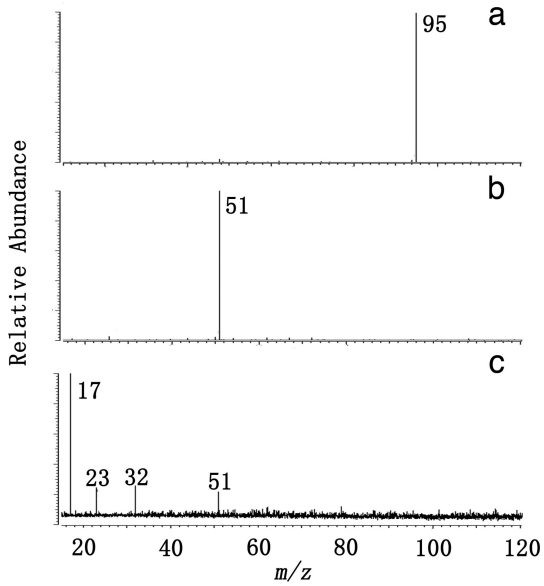


Fig. 2. Generation of LiO^-. (*a*) ESI of lithium oxalate and isolation of the resulting $LiC_2O_4^-$ (*m/z* 95) ion. (*b*) Formation and isolation of $LiCO_2^-$ (*m/z* 51) by CID of $LiC_2O_4^-$. (*c*) Formation of LiO^- and its reaction products with background amounts of H_2O and O_2 by CID of $LiCO_2^-$.

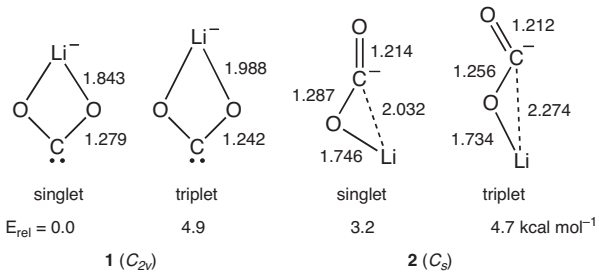


Fig. 3. Computed B3-LYP/6-311+G(2df,2pd) structures for $LiCO_2^-$ and W1 relative energies.

Earlier work on metal salts of dicarboxylate anions (10) suggests that lithium carbonate ($LiCO_3^-$) might be a good precursor for synthesizing LiO^-. The former species was readily generated by ESI, but its fragmentation under a variety of conditions did not afford LiO^- as hoped for. Instead, signal loss was observed.

$$LiOCO_2^- \xrightarrow{CID} LiO^- + CO_2 \qquad [7a]$$

$$\longrightarrow \text{signal loss} \qquad [7b]$$

Lithium oxalate ($LiC_2O_4^-$, *m/z* 95) was subsequently examined because it could lose carbon dioxide followed by carbon monoxide to afford the target species. This sequence indeed takes place as anticipated (Fig. 2), with the lithium salt of doubly deprotonated formic acid ($LiCO_2^-$, *m/z* 51) being initially formed.

$$\underset{m/z\ 95}{LiO{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O^-} \xrightarrow{CID} \underset{m/z\ 51}{LiO{-}\overset{O}{\overset{\|}{C}}{}^-} + CO_2 \qquad [8]$$

This ion also can be viewed as a CO_2 solvate of lithium anion, and was briefly explored.

Computations indicate two low-lying structures for $LiCO_2^-$ (Fig. 3), both of which have small singlet–triplet gaps. At the highest level of theory used (W1), the most stable form of $LiCO_2^-$ is a four-membered ring structure with C_{2v} symmetry in which lithium bridges the two oxygen atoms (**1**). This species is predicted to be a ground-state singlet with a low-lying triplet (Table S1).

The lithium salt of doubly deprotonated formic acid reacts with carbonyl sulfide via sulfur-atom abstraction,

$$\mathrm{LiO{-}C^{-}} \xrightarrow{\mathrm{COS}} \mathrm{LiO{-}\overset{O}{\overset{\|}{C}}{-}S^{-}} + \mathrm{CO} \qquad [9]$$

m/z 83

whereas electron transfer and lithium-anion transfer take place with carbon disulfide.

$$\mathrm{LiO{-}C^{-}} \xrightarrow[35\%]{\mathrm{CS_2}} \mathrm{CS_2^{-}} + \mathrm{LiCO_2} \qquad [10a]$$

m/z 76

$$\xrightarrow[65\%]{} \mathrm{LiCS_2^{-}} + \mathrm{CO_2} \qquad [10b]$$

m/z 83

These results suggest that the electron binding energy of **1** lies between the electron affinities of COS (0.46 ± 0.2 eV) (3) and CS_2 (0.58 ± 0.05 eV) or 0.52 ± 0.12 eV (1 eV = 23.06 kcal or 96.5 kJ). This is consistent with the computed W1 prediction of 0.55 eV.

Lithium monoxide anion was produced by collision-induced dissociation of $LiCO_2^-$,

$$\mathrm{LiO{-}C^{-}} \xrightarrow{\mathrm{CID}} \mathrm{LiO^{-}} + \mathrm{CO} \qquad [11]$$

m/z 51 $\qquad$ m/z 23

but this step is inefficient and difficult to carry out. The desired ion reacts rapidly with adventitious traces of water and molecular oxygen (Fig. 2), and this is exacerbated by the high pressure ($\approx 10^{-6}$ to 10^{-5} torr) of argon that is introduced into the instrument to carry out the CID step. Positive identification of LiO^- was nevertheless confirmed by measuring its exact mass [i.e., m/z 23.01151 (observed) vs. m/z 23.01147 (calculated)], and although its reactivity was difficult to probe, the ion was found to transfer an electron to O_2. This observation indicates that $0 < EA(LiO^{\cdot}) \leq EA(O_2)$, and because $EA(O_2) = 0.448 \pm 0.006$ eV (3), it follows that $EA(LiO^{\cdot})$ is between 0 and 0.45 eV. This is similar to $EA(CsO^{\cdot}) = 0.135 \pm 0.025$ eV (17), which was determined by negative ion photoelectron spectroscopy. High-level theoretical predictions for $EA(LiO^{\cdot})$ of 0.43 [BD(T)], 0.43 (W1), 0.43 (W2C), and 0.39 (CAS-AQCC/aug-cc-pVQZ, which will be referred to as CAS-AQCC hereafter; see *Theoretical Procedures*) eV (Table S2) indicate that the electron affinity is at the upper end of the experimental range.

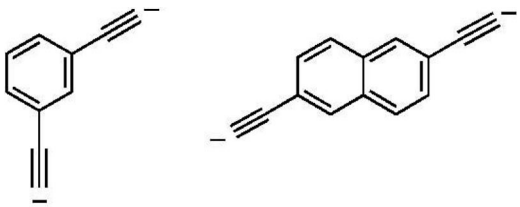
The acidity of lithium hydroxide can be obtained by combining the experimental EA of $LiO^{\cdot}$ with the LiO–H bond dissociation energy as in Eq. **1**. To the best of our knowledge, BDE(LiO–H) has not been reported, but the heats of formation of LiOH (−56.0 ± 1.5 kcal·mol^{-1}) (3, 18, 19) and $LiO^{\cdot}$ (9.1 ± 3.0 kcal·mol^{-1}) (20–25) are known. This leads to BDE(LiO–H) = 117.2 ± 3.4 kcal·mol^{-1}, which is somewhat lower than our theoretical values of 121.1 [BD(T)], 122.4 (W1), 122.2 (W2C), and 121.4 (CAS-AQCC) kcal·mol^{-1}. The difference between experiment and theory can largely be attributed to the heat of formation of $LiO^{\cdot}$, which is directly computed via the theoretical atomization energy to be 12.4 (W1), 12.9 (W2C), and 12.5 (CAS-AQCC) kcal·mol^{-1}. (The atomization energy is the energy required to break a molecule into its constituent atoms, and the theoretical atomization energy can be combined with experimental heats of formation for the atoms to obtain a molecular heat of formation.) Given the general accuracy of these methods and the agreement among their predictions on the one hand, and the uncertainty in the experimental value on the other, it is likely that the heat of formation of $LiO^{\cdot}$ is ≈12.6 kcal·mol^{-1}. Nevertheless, the experimentally derived bond energy can be combined with the experimental electron affinity of $LiO^{\cdot}$ (5.1 ± 5.1 kcal·mol^{-1}) to afford $\Delta H^{\circ}_{acid}(LiOH) = 425.7 \pm 6.1$ kcal·mol^{-1}, which is virtually identical to the direct high-level theoretical predictions of 425.0 [BD(T)], 426.3 (W1), 426.0 (W2C), and 426.2 (CAS-AQCC) kcal·mol^{-1}. We assign a best estimate of 426 ± 2 kcal·mol^{-1}. Thus, lithium hydroxide is a weaker acid than methane ($\Delta H^{\circ}_{acid} = 416.8 \pm 0.7$ kcal·mol^{-1}), and LiO^- is the strongest gas-phase base currently known.

Can an even stronger base be generated in the gas phase? To address this question, BD(T) and CAS-AQCC acidities were computed for $LiBH_2$, $LiCH_3$, $LiNH_2$, LiOH, LiSH, LiH, BeH_2, BH_3, Li_2BH, Li_2CH_2, Li_2NH, $NaCH_3$, NaOH, and NaSH (Table 1 and Table S3). We find that of these molecules only LiOH is less acidic than methane at both computational levels, although Li_2NH and NaOH are found to be very similar to CH_4. Thus, our calculations do not reveal any stronger monoanionic base than LiO^-, despite examining the most logical contenders.

To probe the possible existence of multiply charged anions of greater base strength than LiO^-, we begin with a simplified model that notes that charge–charge repulsion in a doubly charged negative ion (X^{2-}) results in an increased proton affinity ($\Delta PA = PA[X^{2-}] - PA[HX^-]$) but a decreased electron binding energy ($\Delta EBE = EBE[HX^-] - EBE[X^{2-}]$). If one assumes that the increase in the PA due to the Coulombic interactions is exactly counterbalanced by the decrease in the EBE—i.e., $PA[X^{2-}] - PA[HX^-] = EBE[HX^-] - EBE[X^{2-}]$ and therefore $PA[X^{2-}] = EBE[HX^-] + PA[HX^-] - EBE[X^{2-}]$—then the upper limit for the proton affinity of a doubly charged anion can be estimated by summing the PA and EBE of a monoanion. This is the case because $EBE[X^{2-}]$ typically must be greater than zero to be observed (26).

The maximum proton affinity of a dicarboxylate based on this model is 423.0 ± 2.2 kcal·mol^{-1} if the acidity of acetic acid [$\Delta H^{\circ}_{acid}(CH_3CO_2H) = 348.1 \pm 2.2$ kcal·mol^{-1}] and the EBE of acetate [$EA(CH_3CO_2^{\cdot}) = 74.9 \pm 0.2$ kcal·mol^{-1}] are used (3). A similar value of 422.9 ± 2.5 kcal·mol^{-1} is obtained if one uses $\Delta H^{\circ}_{acid}(C_6H_5CO_2H) = 340.1 \pm 2.2$ kcal·mol^{-1} (3) and $EA(C_6H_5CO_2^{\cdot}) = 82.8 \pm 1.2$ kcal·mol^{-1} (27). Likewise, a maximum value of 425.6 ± 8.2 kcal·mol^{-1} is obtained for a disulfonate [$R(SO_3^-)_2$], given $\Delta H^{\circ}_{acid}(C_6H_5SO_3H) = 310.3 \pm 6.8$ kcal·mol^{-1} and $EA(C_6H_5SO_3^{\cdot}) = 115.3 \pm 4.6$ kcal·mol^{-1} (3). Diacetylides [$R(C{\equiv}C^-)_2$] are predicted to be even more basic ($PA \leq 446.4 \pm 0.5$ kcal·mol^{-1}) because acetylene is a relatively weak acid [$\Delta H^{\circ}_{acid}(C_2H_2) = 378.3 \pm 0.1$ kcal·mol^{-1}] (14) and $HC{\equiv}C^{\cdot}$ has a large electron affinity (68.12 ± 0.46 kcal·mol^{-1}) (3). These results suggest that dicarboxylates and disulfonates can approach the basicity of LiO^- and that a diacetylide might exceed it, but they are based on a crude electrostatic model. In reality, the EBE is expected to decrease faster than the proton affinity increases because of electron delocalization in the radical anion that forms upon the loss of an electron from the dianion. As a result, the predicted maximum values for the proton affinities are apt to be too large.

To examine this further, B3-LYP/6-311+G(2df,2pd) calculations were carried out on doubly deprotonated 1,3-diethynylbenzene (**3**) and 2,6-diethynylnaphthalene (**4**).



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The resulting proton affinities for **3** and **4** are 429.4 and 417.8 kcal·mol^{-1}, respectively, and their respective electron binding energies are −3.3 and +1.0 kcal·mol^{-1}. B3-LYP/6-311+G(2df,2pd) computations also were carried out on acetylide (HC≡C$^-$), and as expected the calculated PA (377.8 kcal·mol^{-1}) and EBE (71.6 kcal·mol^{-1}) are in good accord with experiment. As a result, PA(**3**) − PA(HC≡C$^-$) = 51.6 kcal·mol^{-1} and PA(**4**) − PA(HC≡C$^-$) = 40.0 kcal·mol^{-1}, whereas EBE(HC≡C$^-$) − EBE(**3**) = 74.9 kcal·mol^{-1} and EBE(HC≡C$^-$) − EBE(**4**) = 70.6 kcal·mol^{-1}. These results show that the EBE of a dianion falls off more rapidly than its proton affinity as anticipated, and that the crude electrostatic model above overestimates the proton affinities of multiply charged anions. Our findings also suggest that it will be difficult to produce a diacetylide with a PA in excess of ≈426 kcal·mol^{-1} (i.e., 429.4–3.3 kcal·mol^{-1}) and that "the sky is not the limit" when it comes to designing multiply charged anions that are both highly basic and observable (i.e., have a positive EBE). Consequently, it will be a challenge to find a competitor for LiO$^-$ even if multiply charged anions are considered, and lithium hydroxide will be hard to replace at the top of the gas-phase acidity scale.

Conclusions

Lithium is an interesting substituent that can dramatically alter the structure, ground-state multiplicity, and basicity of negative ions. In some instances it is acid-enhancing, whereas in others it is acid-weakening. Compared with the first-row hydrides CH_4 to HF, the acidities of lithiated analogs display the opposite trend with respect to electronegativity. A more covalent (softer) Li–X bond leads to greater acidity, whereas a more ionic (harder) bond leads to weaker acidity. Lithium oxalate is a suitable precursor for the generation of LiO$^-$, and observation of electron transfer from the latter to O_2 has enabled us to determine that its electron binding energy lies between 0 and 10.3 kcal·mol^{-1} or 5.1 ± 5.1 kcal·mol^{-1}. By combining this quantity with ΔH°_f(LiO$^\cdot$), ΔH°_{acid}(LiOH) = 425.7 ± 6.1 kcal·mol^{-1} was derived. High-level *ab initio* calculations also were carried out and predict that ΔH°_{acid}(LiOH) = 425.9, EA(LiO$^\cdot$) = 9.7, and BDE(LiO–H) = 121.8 where these values are in kcal·mol^{-1} and represent the average of the BD(T)/aug-cc-pVQZ, W1, W2C, and CAS-AQCC/aug-cc-pVQZ results. Consequently, lithium hydroxide is found to be the weakest acid known in the gas phase, and LiO$^-$ is the strongest base. Computations on a variety of additional species do not reveal any rivals to LiOH at the top of the gas-phase acidity scale, and a simple electrostatic model suggests that it will be difficult to prepare a multiply charged anion that is both more basic than LiO$^-$ and bound with respect to electron detachment.

Materials and Methods

Gas-Phase Experiments. A Fourier transform mass spectrometer (FTMS) consisting of an IonSpec ESI cart with a gold-plated cylindrical cell and a 3-T superconducting magnet was controlled by a PC running the Omega 2004 software package. Lithiated ions were prepared by spraying 200–500 μM solutions of lithium carbonate or a 1:3 mixture of oxalic acid and lithium hydroxide in 3:1 (vol/vol) mixtures of methanol and water at a flow rate of 10 μl/min into a Z-spray (Micromass) ESI source. The resulting anions were extracted into a hexapole to build the signal intensity and then were transported into the FTMS cell via a radio frequency-only quadrupole ion guide (28). A pulse of argon was used to facilitate the trapping of the ions in the FTMS cell and also served to vibrationally relax them (29, 30). Lithium carbonate (*m/z* 67) and lithium oxalate (*m/z* 95) were isolated by using an arbitrary waveform excitation (31) and subsequently fragmented upon energetic collisions with a pulse of argon at a nominal energy of 3.5 eV. In the latter case, the resulting $LiCO_2^-$ ion (*m/z* 51) was allowed to react with various reagents as a function of time, or alternatively it was broken apart in a second on-resonance CID step using another pulse of argon and a laboratory energy of ≈3.5 eV to afford LiO$^-$ (*m/z* 23). The reactivity of this ion was probed too, but this was difficult because of the relatively poor signal-to-noise ratio. LiO$^-$ also reacts rapidly with H_2O and O_2, both of which are ubiquitous impurities and contaminants that cannot be entirely eliminated. This problem is exacerbated by pulsing large amounts of argon into the vacuum system to trap the ions and then fragment them even though the transfer lines were baked out and reagent-grade argon (99.998%) was used. Exact masses of all of the ions studied herein were determined, nevertheless, and this was particularly valuable for differentiating ions containing two oxygens versus one sulfur atom.

Theoretical Procedures. Calculations were carried out at the G3 (32), BD(T)/aug-cc-pVQZ (33, 34), W1 (35, 36), W2C/AA′WCVnZ (19), and CAS-AQCC/aug-cc-pVQZ (37, 38) levels by using Gaussian 03 (39) and Molpro 2006 (40). The W2C/AA′WCV5Z level of theory differs from the standard W2C procedure (19) in that AA′WCV*n*Z (aug,aug′-cc-pWCV*n*Z) basis sets are used instead of A′WCV*n*Z (aug′-cc-pWCVnZ) basis sets. The difference between these two types of basis sets is that the AA′WCV*n*Z basis sets have diffuse functions on all nonhydrogen atoms, whereas the A′WCV*n*Z basis sets do not have diffuse functions on hydrogen, alkali metals, or alkaline-earth metals. This refinement is potentially important for the anions involving alkali metals, which are the principal focus of the present study. For the G3, BD(T), and CAS-AQCC calculations, we have examined a number of electronic states to obtain the state of lowest energy. BD(T) and W1 calculations were carried out with B3-LYP/6-31G(2df,p)- and B3-LYP/cc-pVTZ+d-optimized geometries, respectively. For W2C calculations, geometries were initially obtained at the B3-LYP/A′WCV5Z level and subsequently refined at the CCSD(T)/A′WCV5Z level. The B3-LYP geometries were used for frequency calculations, and single-point energies were obtained by using the CCSD(T) geometries. The CAS-AQCC calculations were performed with a full-valence correlation space by using B3-LYP/6-31G(2df,p)-optimized geometries. CCSD(T) single-point energies were computed in a few instances with the AA′VTZ basis set. All of the resulting energies are reported as enthalpies at 298 K and include zero-point vibrational energies and thermal enthalpy corrections obtained by using scaled HF/6-31G(d) (0.8929, G3), B3-LYP/6-31G(2df,p) [0.9854, BD(T), and CAS-AQCC], B3-LYP/cc-pVTZ+d (0.985, W1), or B3-LYP/A′WCV5Z (0.985, W2C) vibrational frequencies (35, 41, 42). Some B3-LYP optimizations were also carried out with the AA′VTZ and 6-311+G(2df,2pd) basis sets, and the vibrational frequencies used to obtain thermochemical information were also scaled by 0.9854 in these instances. In all cases, weak vibrational modes that contribute >0.3 kcal·mol^{-1} (RT/2) to the thermal energy were replaced by RT/2. There is generally good agreement between the various approaches used in this work and, consequently, the results from only the highest-level procedures are presented in the text. The remaining data are given in Tables S1–S3.

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